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STATISTICAL MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE.(U)
MAY 80 P L TAYLOR, A J HOPFINGER DAAG29-78-G-0064
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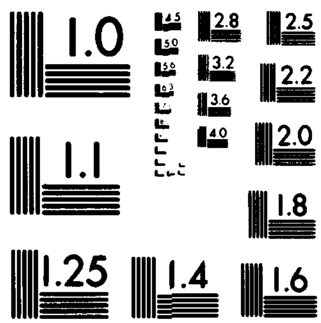

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STATISTICAL MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE

LEVEL II

FINAL REPORT

P. L. TAYLOR AND A. J. HOPFINGER

MAY 15, 1980

U. S. ARMY RESEARCH OFFICE
POST OFFICE BOX 12211
RESEARCH TRIANGLE PARK, NC 27709

DAAG 29-78G-0064
DAAG 29-77G-0018

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: ~~F1~~

2. GOVT ACCESSION NO.: AD-A084 846

3. RECIPIENT'S CATALOG NUMBER: (9) Rept.

4. TITLE (and Subtitle): (6) Statistical Mechanical Study of Polyvinylidene Fluoride.

5. TYPE OF REPORT & PERIOD COVERED: FINAL, Apr [redacted] 77-Mar [redacted] 80

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) Philip [redacted] L./Taylor [redacted] Anton J./Hopfinger

8. CONTRACT OR GRANT NUMBER(s): DAAG 29-78G-0064; DAAG 29-77G-0018

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Case Western Reserve University, Cleveland, Ohio 44106

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709

12. REPORT DATE: (11) 15 May [redacted] 80

13. NUMBER OF PAGES: 7

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

(18) ARO (19) 14602.2-P

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

(12) 9

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

(15) DAAG29-78-G-0064, DAAG29-77-G-0118

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polyvinylidene fluoride
Piezoelectricity

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A theoretical study of polyvinylidene fluoride has been performed in which calculations have been made of the equation of state, of the piezo-electric and pyroelectric coefficients, and of the mechanism of poling of β-phase material. Transfer-integral and mean-field methods have been used → over

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) to derive the free energies of the various phases, and thence to derive the thermodynamic variables as functions of temperature, stress, and applied electric field. The poling process whereby electrical activity is induced in β-phase material has been studied in a model in which solitary waves of rotation are induced by temperature and applied electric fields and propogate along a chain axis. The rate of spontaneous creation of these kinks of polarization and their velocity have been used to predict the times necessary for poling material under various conditions.

FINAL REPORT

The performed research consisted of a theoretical study of both equilibrium and non-equilibrium properties of poly(vinylidene fluoride), hereafter referred to as PVF_2. This material can exhibit strong piezoelectric and pyroelectric effects if suitably prepared, and is consequently of great technological interest. The study consisted of a series of calculations of the equation of state, and the mechanism by which electrical activity is induced.

Detailed accounts of the results of our investigations have been given in Refs. 1-9, and so we here just provide a brief summary of some of the more important aspects of our work.

(i) <u>Equation of state and crystal structures</u>

The free energy of an assembly of interacting chains of PVF_2 was calculated in a formalism whose starting point was close to first principles. The potential energies of interaction of various pairs of atoms were calculated by using molecular orbital techniques and molecular mechanics, and these potentials were then used in a study of the statistical mechanics of an assembly of interacting chains. The basic technique involved the precise solution of a model of a single chain in a potential field that was expressed as a mean-field approximation to the true interchain potential. The resulting set of equations was solved self-consistently to yield the Helmholtz and Gibbs energies.

A rich variety of phases emerged from this calculation, and it was gratifying that the phase predicted to be most stable was indeed the phase-II, or α-phase, crystal structure. Of the other phases found in this work the β phase was predicted to have a higher free energy than the α phase, and thus to be only metastable; application of a unaxial stress, however, was found to lower the free energy of the β phase sufficiently to make it the most stable, in accord with experiment. These results are central to our studies of PVF_2, and are described in detail in Refs. 1 and 2.

Other work related to the stability and existence of various crystal structures includes some studies[3,4] of possible conformations for the phase-III form of PVF_2, and a general review of the application of our transfer-integral techniques to polymer properties[5]. Some of the support for this aspect of our research was received from the N.S.F. Materials Research Laboratories at Case, in addition to the principal support from the A.R.O.

(ii) Piezo- and pyroelectric coefficients

The large observed piezoelectric effects in PVF_2 have been conjectured to arise from a variety of causes[10]. Of these we have studied in particular the contributions from changes in shape of a sample under stress (that is, the second piezoelectricity) and from effects at the boundary between amorphous and β-phase material. While secondary effects can explain much of the observed coefficient, there appears to remain a further component requiring an alternative explanation, and to this end we have looked at a model in which stress-induced reversible crystallization can enlarge the size of a β-phase crystallite at the expense of amorphous material[6].

In the course of this study it was discovered that the thermodynamics of piezoelectric devices involving polymers does not appear to be completely understood. Contributions to the free energy arising from size changes of an electrode plated to a polymer film can produce forces that are absent from most treatments of piezoelectric devices. While these forces may produce negligible effects in ceramic ferroelectrics they can apparently be significant in a comparatively soft polymer, and need careful treatment[7].

(iii) Poling of PVF_2

The production of piezoelectric material by annealing β-phase film in a large electric field has been studied in a model in which a reorientation occurs of the zigzag planar chain about its axis. The equations of motion for this process are highly nonlinear, and lead to consideration of a propagating solitary wave of polarization. These "kink" solutions have been studied in a model in which the chain rotates by 180° about its axis[8] and also in one in which a 60° rotation occurs, accompanied by a small change in lattice dimensions[9], as had been suggested by Kepler and Anderson. The model involving rotation by 60° gives the better agreement with experimentally observed poling times.

References

1. N. C. Banik, F. P. Boyle, T. J. Sluckin, P. L. Taylor, S. K. Tripathy and A. J. Hopfinger, Phys. Rev. Letters, 43, 456 (1979).
2. N. C. Banik, F. P. Boyle, T. J. Sluckin, P. L. Taylor, S. K. Tripathy and A. J. Hopfinger, submitted to J. Chem. Phys.
3. S. K. Tripathy, R. Potenzone, Jr., A. J. Hopfinger, N. C. Banik, and P. L. Taylor, Macromolecules, 12, 656 (1979).
4. N. C. Banik, P. L. Taylor, S. K. Tripathy, and A. J. Hopfinger, Macromolecules, in press.
5. A. J. Hopfinger and P. L. Taylor, Accounts of Chemical Research, 12, 217 (1979).
6. H. Dvey-Aharon, T. J. Sluckin, P. L. Taylor, and A. J. Hopfinger, (in preparation).
7. P. L. Taylor and H. Dvey-Aharon, Thermodynamics of piezoelectricity and pyroelectricity in polymers, (in preparation).
8. A. J. Hopfinger, A. J. Lewanski, T. J. Sluckin and P. L. Taylor in Solitons and Condensed-Matter Physics (Ed. A. R. Bishop and T. Schneider) (Springer, New York), p. 330 (1979).
9. H. Dvey-Aharon, T. J. Sluckin, P. L. Taylor, and A. J. Hopfinger, (in preparation).

List of Publications Supported

Solitary-Wave Propagation as a Model
for Poling in PVF_2
A. J. Hopfinger, A. J. Lewanski,
T. J. Sluckin and P. L. Taylor in
Solitons and Condensed-Matter Physics
(Ed. A. R. Bishop and T. Schneider)
(Springer, New York) 330 1979

Predicted Chain Conformation for a Possible
Phase III Form of Poly(vinylidene Fluoride)
S. K. Tripathy, R. Potenzone, Jr.,
A. J. Hopfinger, N. C. Banik and P. L. Taylor
Macromolecules 12 : 656 1979

Polymer Crystal Transition Theory
A. J. Hopfinger and P. L. Taylor
Accounts of Chemical Research 12 : 217 1979

Theory of Structural Phase Transitions in
Poly(vinylidene Fluoride)
N. C. Banik, F. P. Boyle, T. J. Sluckin,
P. L. Taylor, S. K. Tripathy and A. J. Hopfinger
Phys. Rev. Letters 43 : 456 1979

Chain Conformation of Phase III
Poly(vinylidene Fluoride)
N. C. Banik, P. L. Taylor, S. K. Tripathy
and A. J. Hopfinter
Macromolecules 12 : 1015 1979

Theory of Structural Phase Transitions
in Crystalline Poly(vinylidene Fluoride)
N. C. Banik, F. P. Boyle, T. J. Sluckin,
P. L. Taylor, S. K. Tripathy and
A. J. Hopfinger
J. Chem. Phys. 72 : 3191 1980

Kink Propagation as a Model for Poling
in PVF_2
H. Dvey-Aharon, T. J. Sluckin, P. L.
Taylor and A. J. Hopfinger
Phys. Rev. B (in press) 1980

Field-Induced Phase Transitions in Phase II
Poly(vinylidene Fluoride)
N. C. Banik, P. L. Taylor and A. J.
Hopfinger
App. Phys. Letters 1980

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Frederick Boyle earned the Ph.D. degree in Physics during the tenure of this grant.